

*Reversible Ionic Liquids as
Double-Action Solvents for
Efficient CO₂ Capture*

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Chemical Engineering and Chemistry

Two Decades of Collaboration

- Jointly Directed PhD Students and Postdoctorals
 - ✓ Chemical Engineers
 - ✓ Chemists
 - ✓ > 50 Completed
- >50 Joint Research Grants
- >250 Publications and Presentations
- **2004 Presidential Green Chemistry Challenge Award**

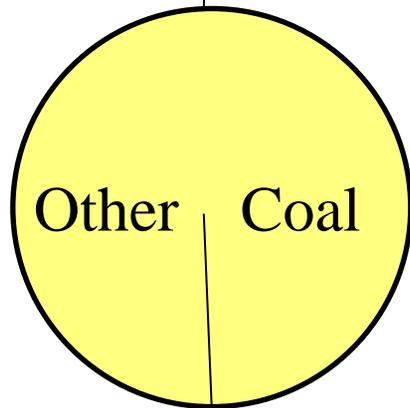


Outline of Presentation

- Introduction – the Need for CO₂ Capture
- Background – Existing Reversible Two-Component Ionic Liquids (RevILs)
- Path Forward –The Upcoming Project
 - ✓ Synthesize and Characterization of New Single-Component RevILs
 - ✓ Determine Reaction Thermodynamics and Rates
 - ✓ Optimize CO₂ Capture Solvent Structure
 - ✓ Process Design and Economic Analysis

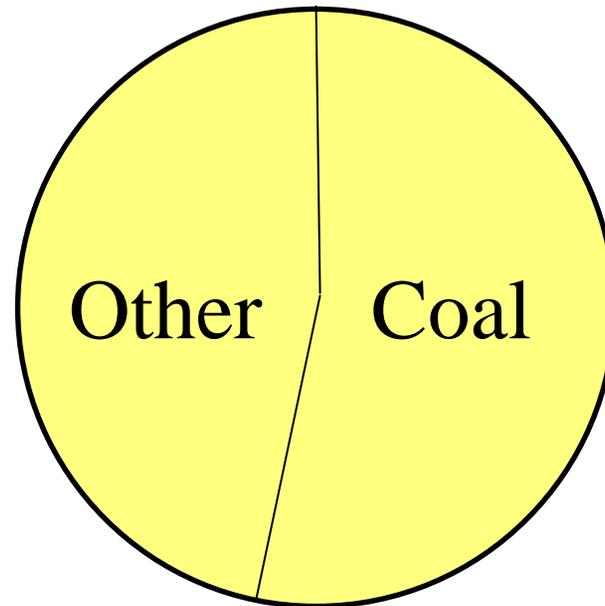
Electricity Generation from Coal Expected to Rise

- Summary of U.S. Electricity Generation:



- 2003 -

3.662 trillion kWhrs

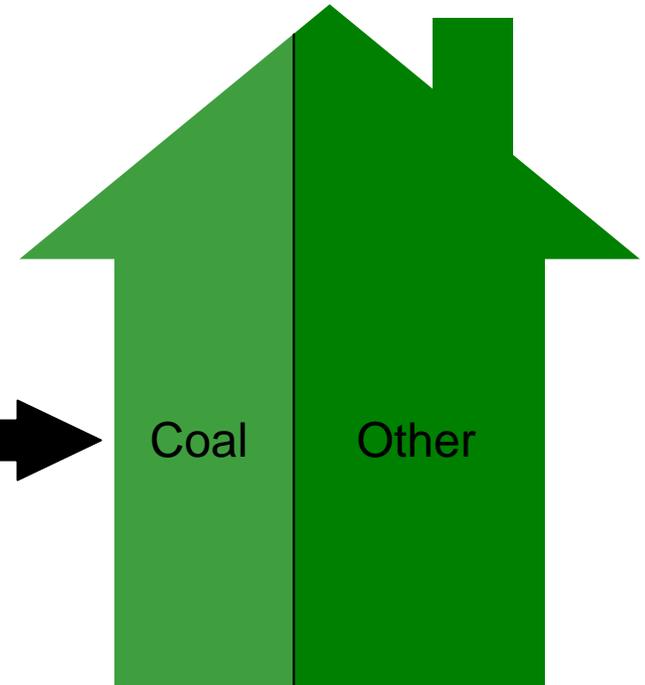


- 2030 -

5.5 trillion kWhrs
(projected)

Coal Combustion is the Leading Contributor to CO₂ Emissions in U.S.

Wyodak 500 MW PC Power Plant – Gillette, WY



- 2003 CO₂ Emissions -
6300 Mt: 1/3 from coal

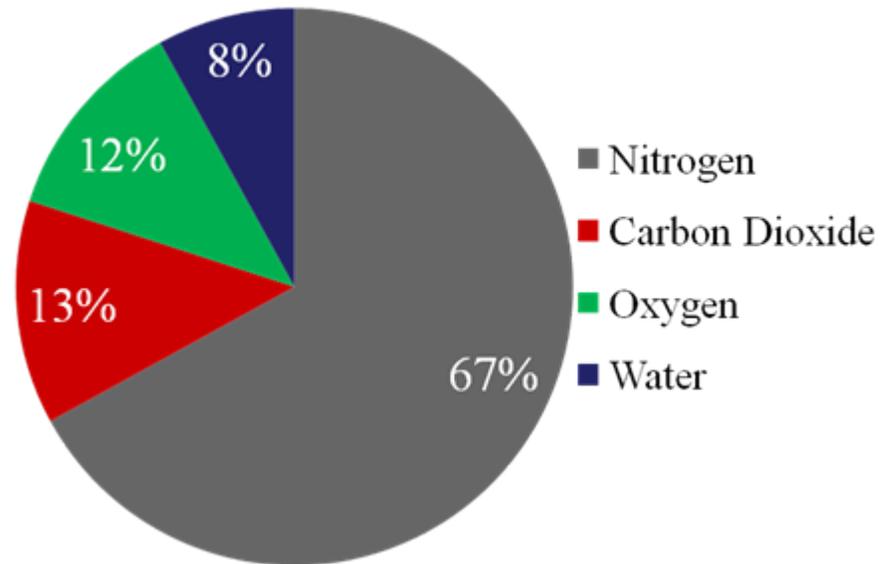
Power Plant Flue Gas:

A Technically Challenging Feed Stream

- 350 MW PC power plant flue gas characteristics:

- ✓ Temp = 185°C
- ✓ Flow = 78 MMscf/hr
- ✓ CO₂ = 6000 t/day

Typical Flue Gas Composition -



- Must Produce a High Purity Product Stream

Basis for Comparison: Monoethanolamine (MEA)

- MEA uses chemical absorption
 - ✓ Similar process design
- Well researched, proven
- Problem:
 - ✓ Dilute solvent streams
 - ✓ High operating costs
- Can validate simulation
- Provides efficiency and economic targets



NewPoint Gas MEA Process

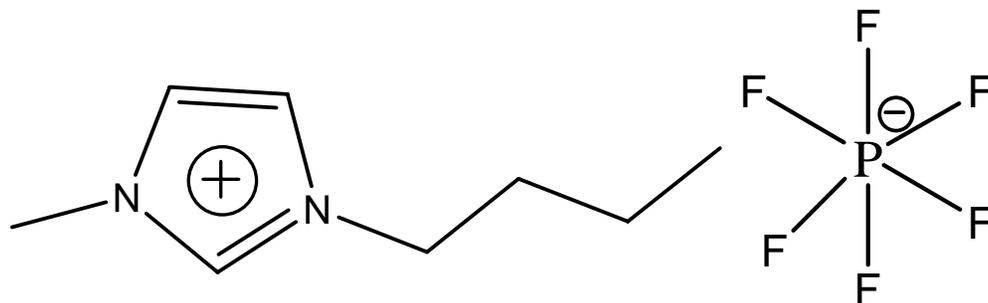
The MEA Process: An Energy Hog

- Computer Simulation
 - ✓ Flue Gas from 350 MW PC Plant
 - ✓ Gives 90% Recovery
 - ✓ Yields 95% CO₂ Product Stream
- Bottom Line: Solvent Regeneration Accounts for About 2/3 of Operating Costs

Background:

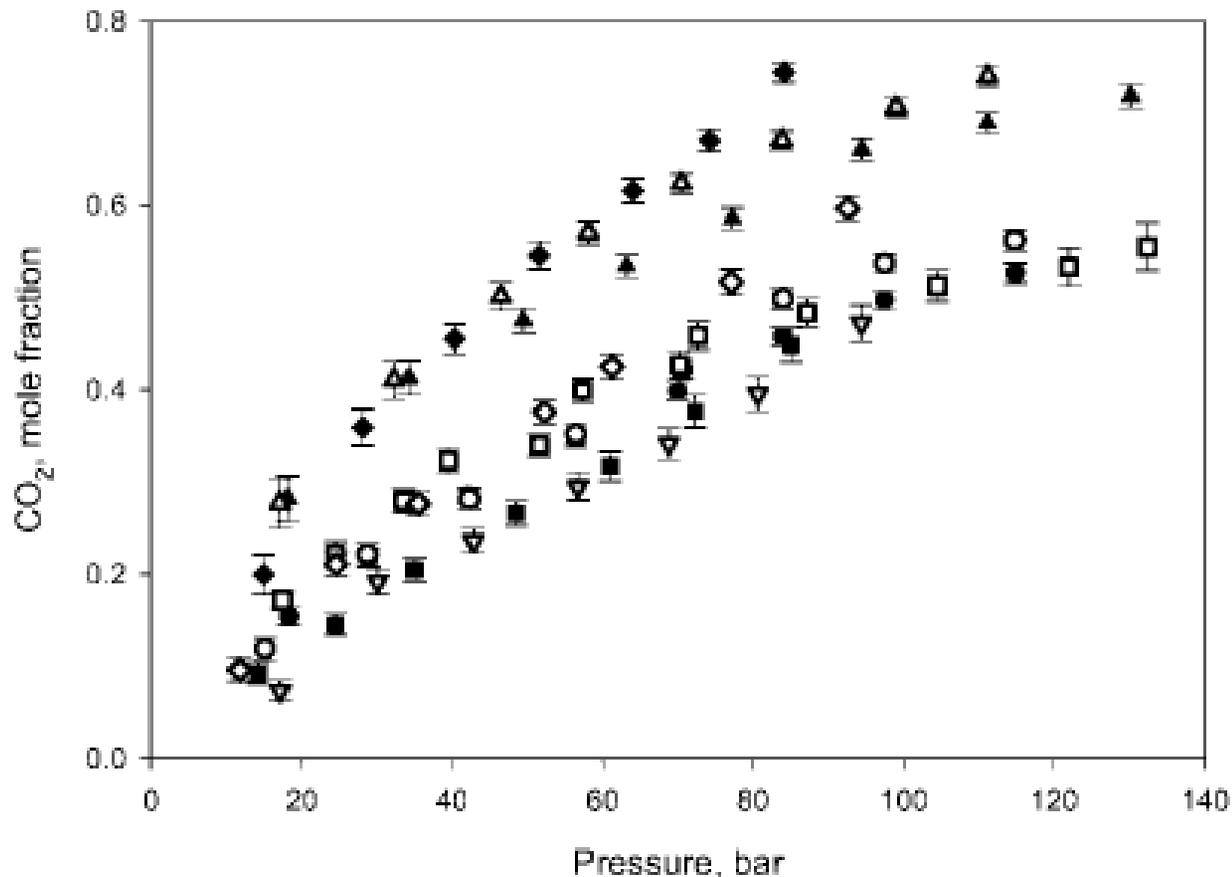
Traditional Ionic Liquids as Solvents

- Low-Melting Salts
 - ✓ Touted as “Green”
 - ✓ “Zero” Vapor Pressure, No Solvent Losses
- Many Organic Reactions Run Successfully
- Can Dissolve Gaseous CO₂
- Separation of Products are Challenging
- Many ILs are Expensive and/or Toxic



CO₂ Capture by Absorption in ILs

DOE, "Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO₂ Capture," Brennecke, Maginn and Schneider



CO₂ Solubility in [bmim]⁺-Based ILs at 333^oK
Brennecke et al., *Acc. Chem. Res.*, **2007**

Mechanisms for CO₂ Capture

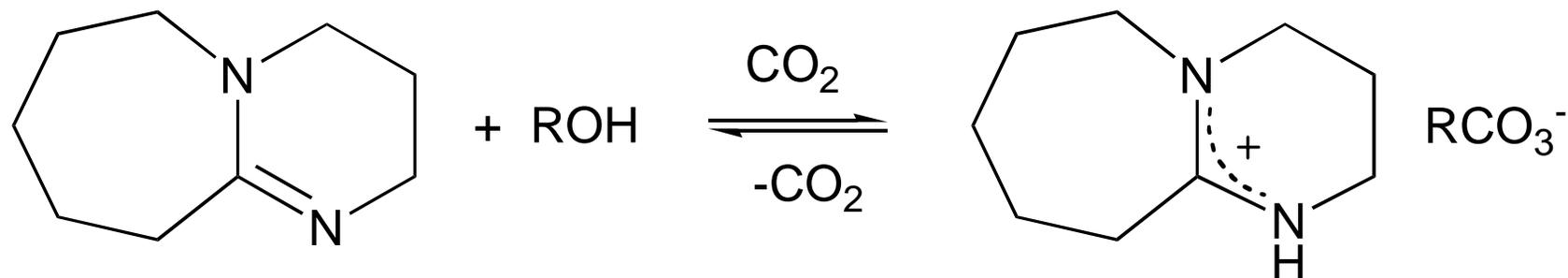
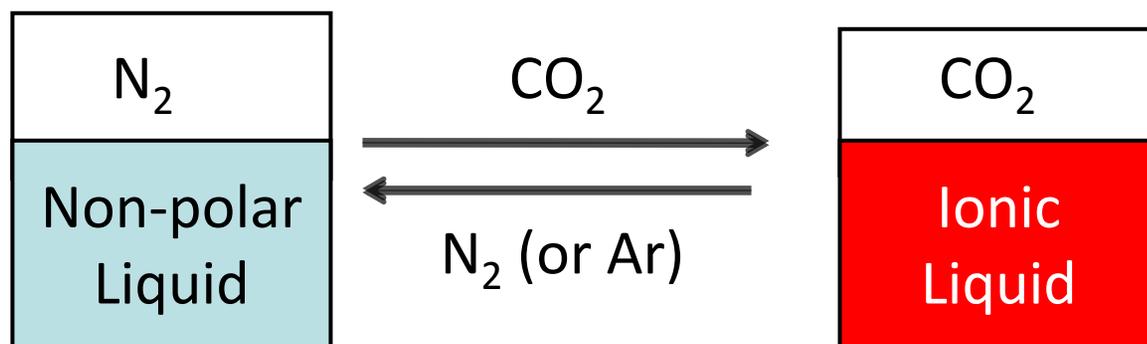
- **Chemical Absorption**

- ✓ Chemical Reaction Affords Capture
- ✓ High Efficiency
- ✓ Thermally Driven Process
- ✓ Large Heat for Regeneration
- ✓ Thoroughly Researched
- ✓ Proven Technology

- **Physical Absorption**

- ✓ van der Waals Forces Give Separation
- ✓ High Capacities and Selectivities Reported
- ✓ Pressure Driven (Typically)
- ✓ Low Heat for Regeneration
- ✓ Economically Unfeasible
- ✓ Not Effective...Alone

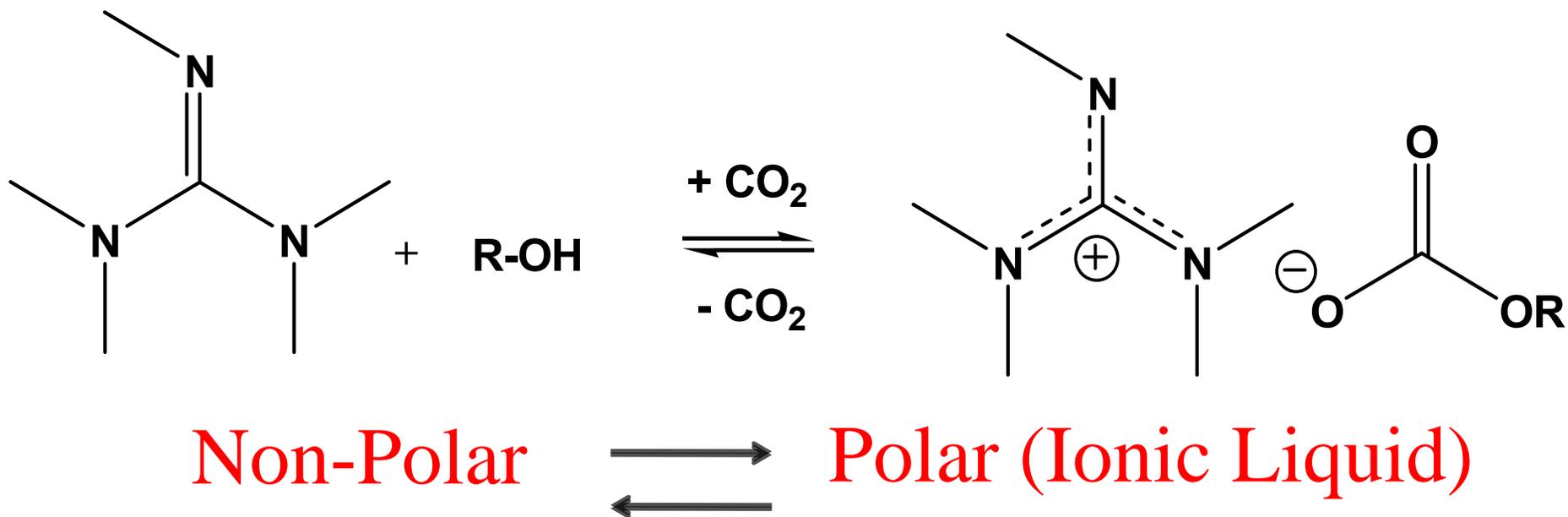
The Path to Dual-Mechanism Capture: Two-Component Reversible CO_2 (1 atm.) Acts as “Switch”



Guanidine-Based Reversible

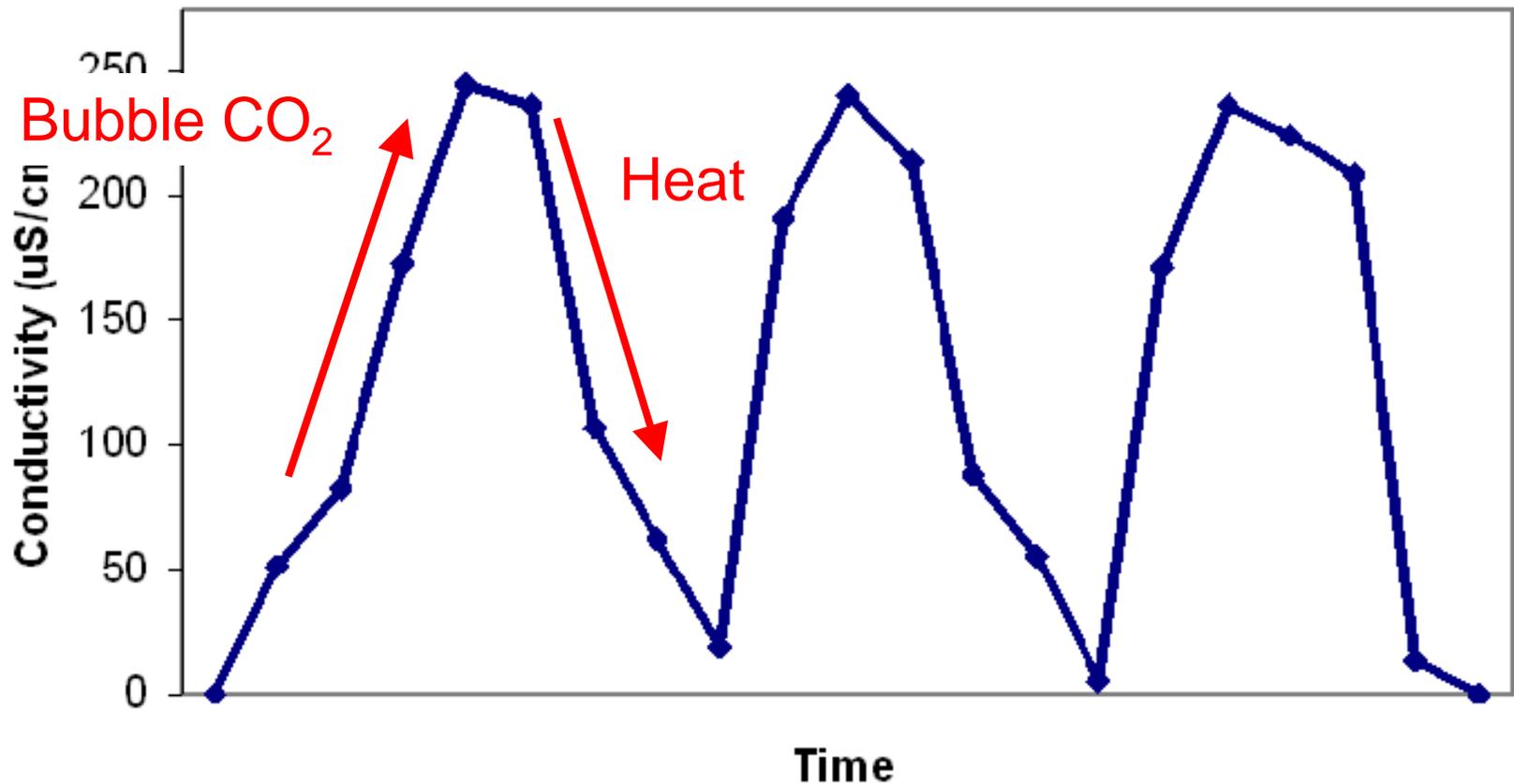
CO₂ (1 atm.) Acts as “Switch”

- **TMBG** (tetramethyl-butyl guanidine)

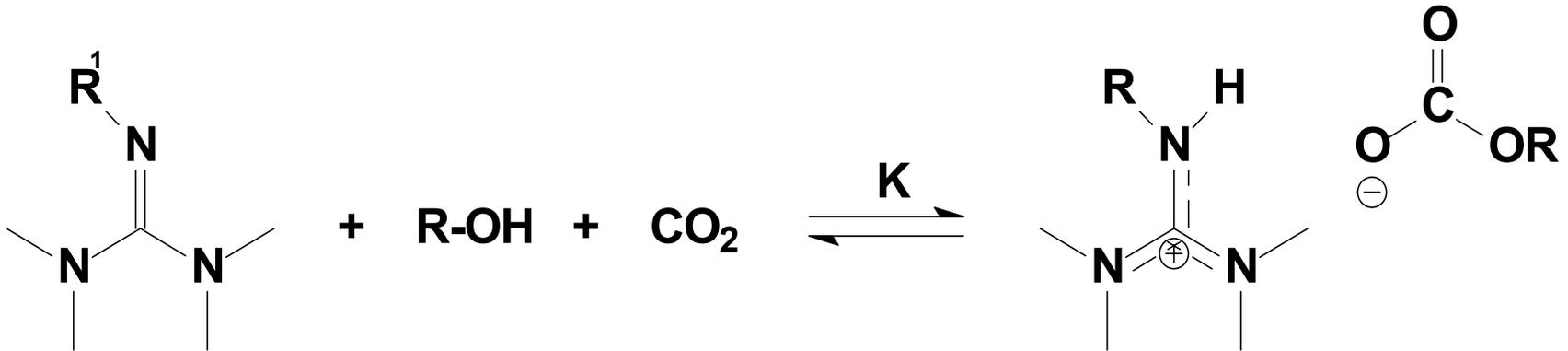


Turning the RevIL “On” and “Off”

- Equimolar methanol/TMBG diluted in chloroform



Thermodynamic Relationships



$$\text{Equilibrium Constant: } K = \frac{\text{CONC}_{\text{IonicLiquid}}}{P_{\text{CO}_2} \text{CONC}_{\text{TMBG}} \text{CONC}_{\text{Alcohol}}}$$

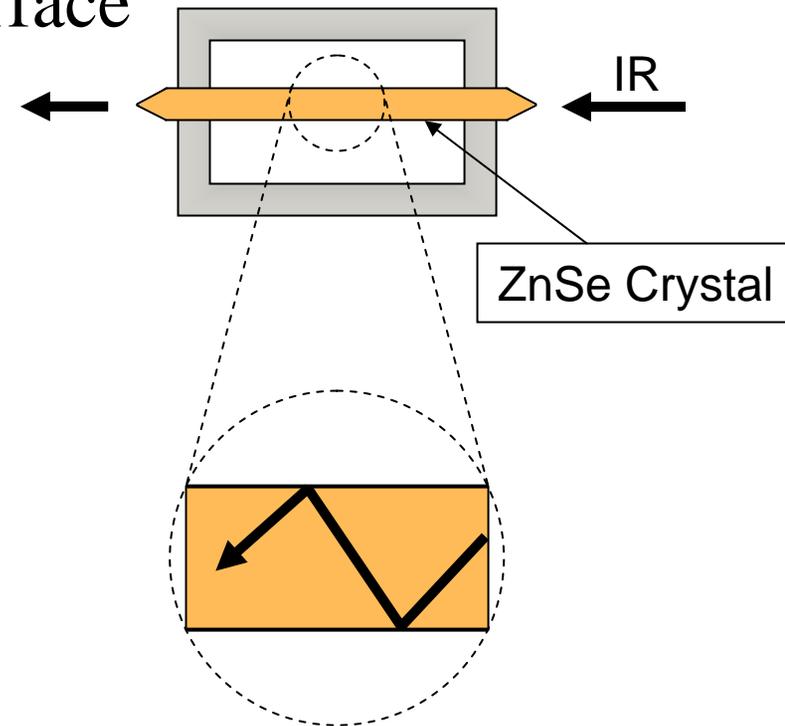
$$\text{Heat of Adsorption: } \frac{d(\ln K)}{dT} = \frac{\Delta H^{\text{abs}}}{RT^2}$$

Thermodynamics – What Do We Want?

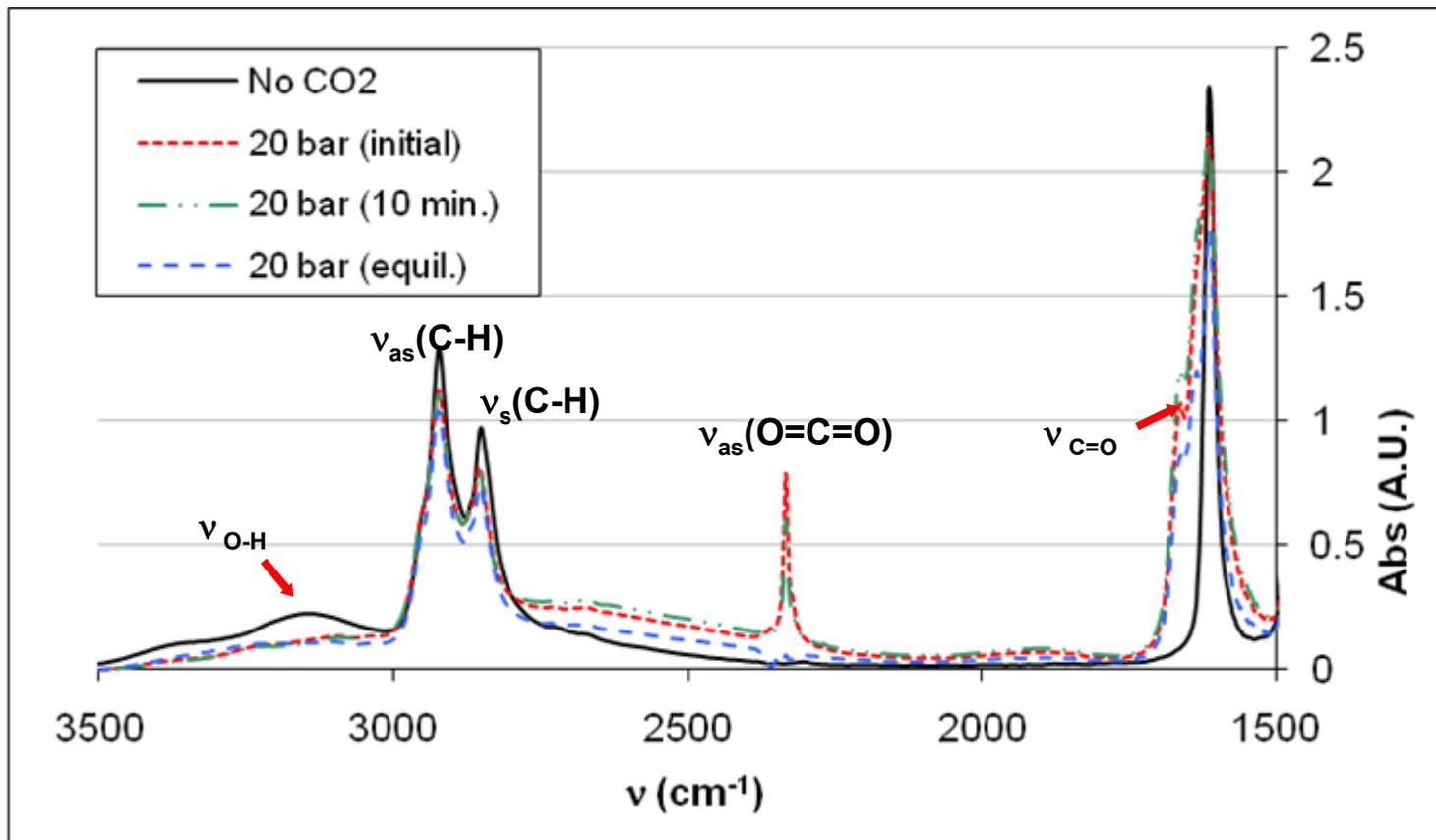
- Low Heat Requirement for Regeneration
- Favorable Equilibrium at T_{low} for Capture
- Favorable Equilibrium at T_{high} for Release
- T_{low} and T_{high} as Close to Each Other as Possible
 - ✓ Reduces Losses in Cycling Solvent
 - ✓ BUT, true only for High Heat of Regeneration
- Bottom Line: Optimize and Engineer

Preliminary Thermo Measurements

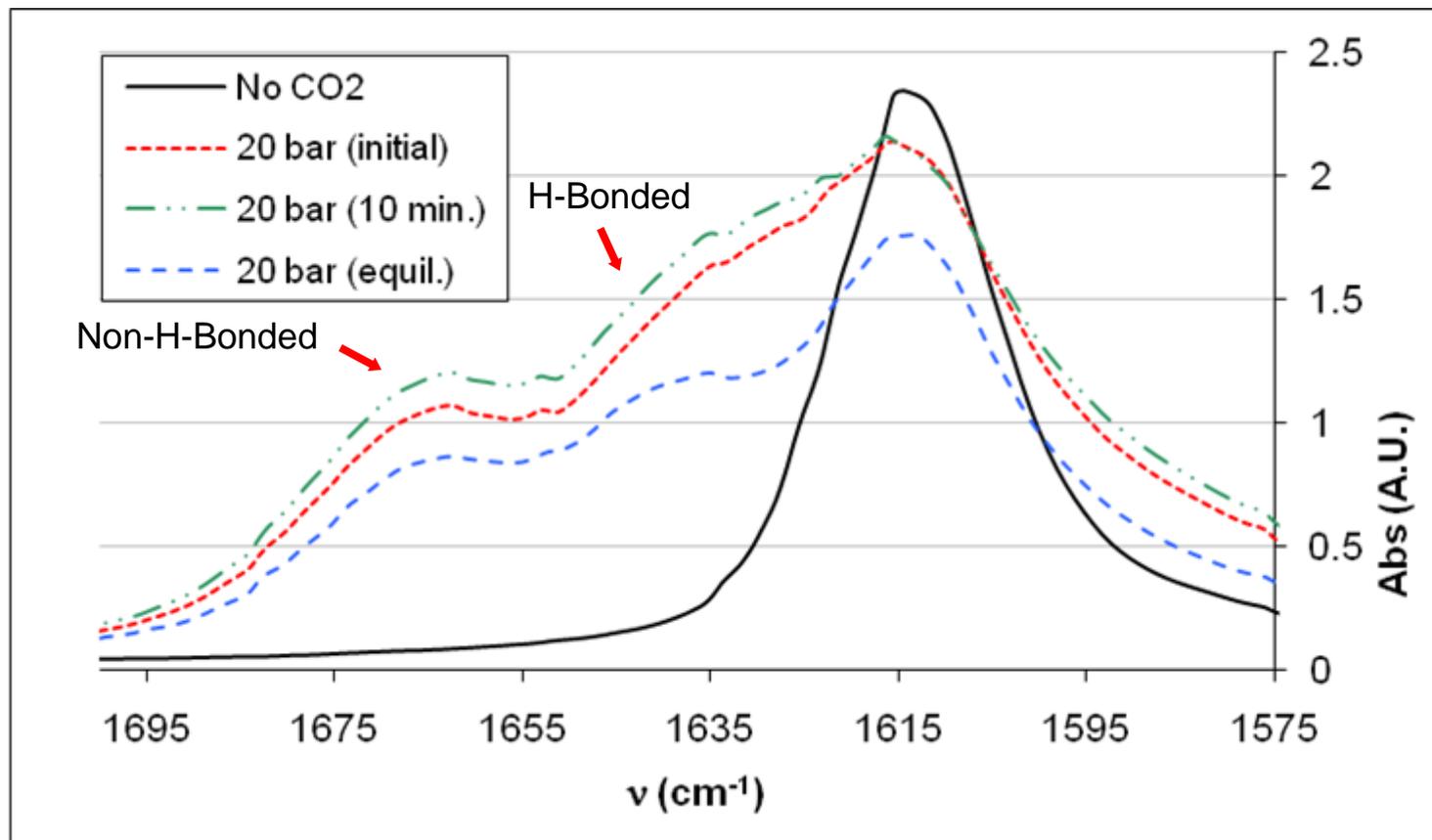
- High-pressure ATR-FTIR cell
 - ✓ Attenuated Total Reflection
 - ✓ IR reflected from sample surface
 - ✓ Pathlength: \sim a few μm



Dynamics of RevIL Formation



Reaction of CO_2 + Alcohol Results in Formation of a Carbonyl



Phases of New DOE Project

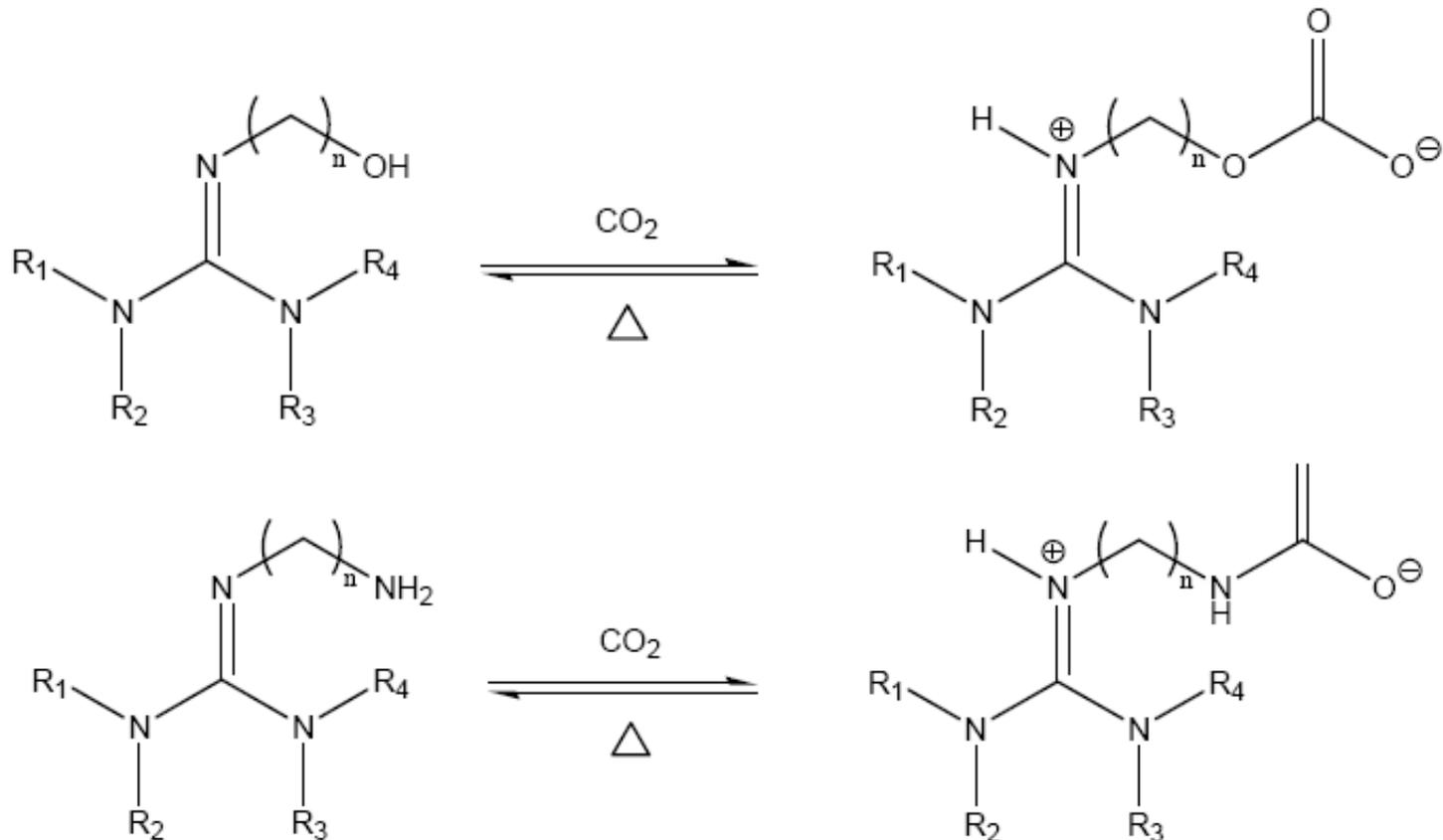
- Synthesize and Characterize Single-Component Silyl RevILs
 - ✓ Amine-Based and Guanidine-Based
 - ✓ Structure/Property Relationships
 - Both Empirical and Theoretical
 - ✓ Directed Design of Molecules for CO₂ Capture
- Thermodynamics, Rates of RevIL Formation
- Optimize CO₂ Capture Solvent Structure
- Process Design and Economic Analysis

Limitations of 2-Component RevLLs

- Too Complex
 - ✓ Must Control Stoichiometry
- Light Alcohol will Evaporate with CO₂
- Heavy Alcohol Has Too Much Heat Capacity
- Too Hard to Control
- Too Much Energy Penalty

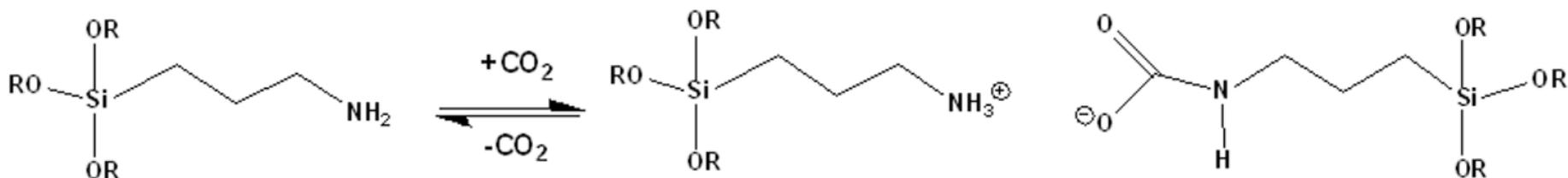
Synthesize and Characterize Single-Component RevILs

- Example Based on Guanidine Molecule



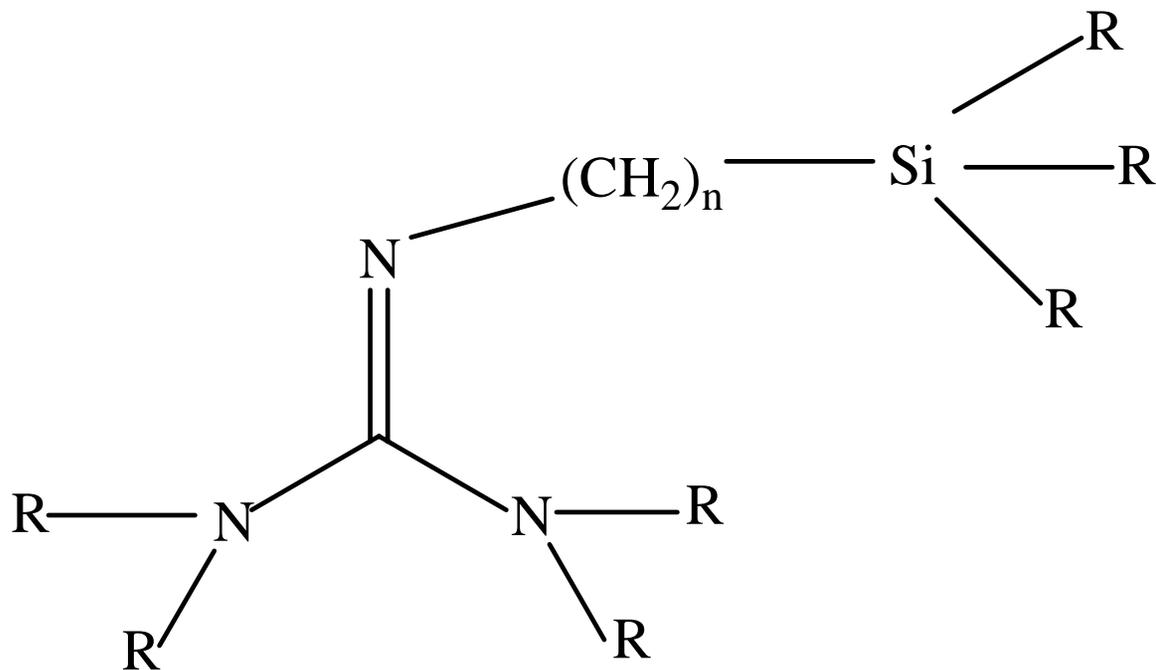
Synthesize and Characterize Single-Component Silyl ReviLs

- Example Based on Silylated Amine
- Structures are Completely Adjustable
- Eliminates Need for Alcohol



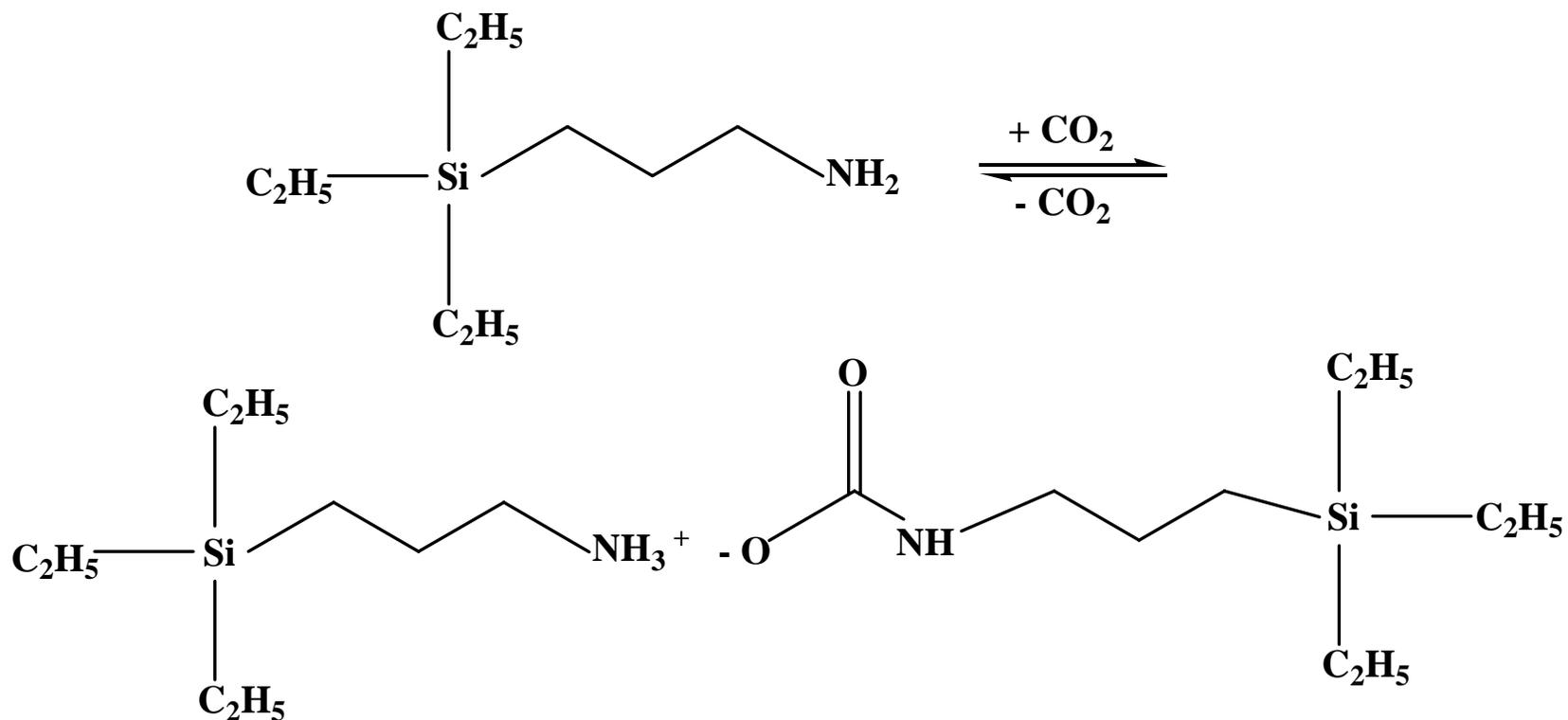
Synthesize and Characterize Single-Component Silyl RevILs

- Example Based on Silylated Guanidine
- Structures are Completely Adjustable
- Eliminates Need for Alcohol



Must Choose Chemistry That Works Well in Presence of Water

- Also Example Based on Silylated Amine
- Change Alkoxy Group to Alkane Group



Single-Component Silyl RevILs

- Our Designer Solvents Use Both Mechanisms
- Chemical Absorption
 - ✓ By Reaction of CO₂ with RevILs
- Physical Absorption
 - ✓ By Dissolution of CO₂ in RevILs
- Increases Capacity
 - ✓ Better Separation with Less Energy Penalty

Interface Structure with Properties

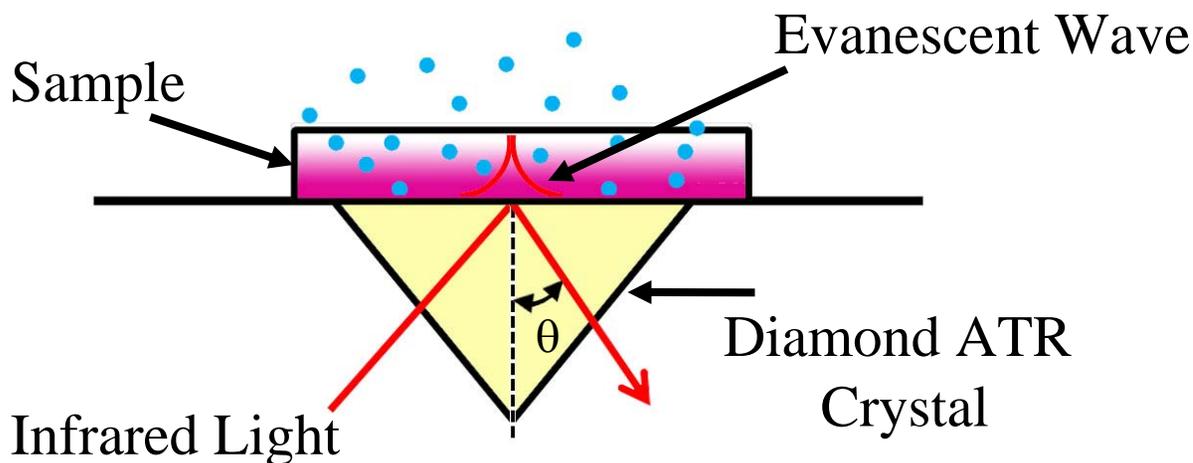
- Measure Equilibrium and Heat of Reaction
- Use Structure/Property Methods to Upgrade
 - ✓ Empirical Methods
 - ✓ Theoretical Methods
- Synthesize Next Generation of RevILs
 - ✓ Improved Properties
- Repeat

Thermodynamics and Rates

- Use Single-Pass Diamond Cell
- Effect of Structure
 - ✓ On Chemical Equilibrium
 - ✓ On Heat of Reaction
 - ✓ On Rates
- Effect of Temperature
- Effect of CO₂ Pressure
- Effect of Water

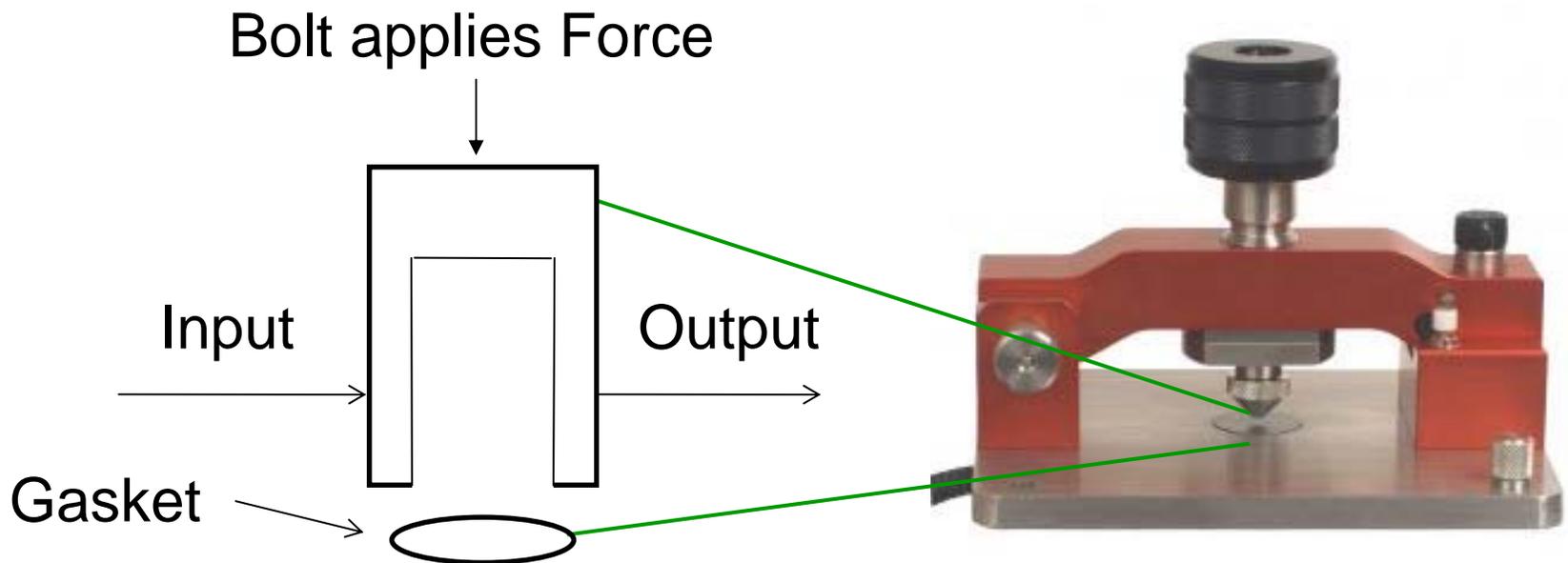
Single-Pass Diamond ATR IR Cell

- Ample Adsorption in Single Pass
- Small Volume – No Transport Limitations
- Temperature-Controlled
- Rapid and Accurate



Sample Cell for ATR on RevILs

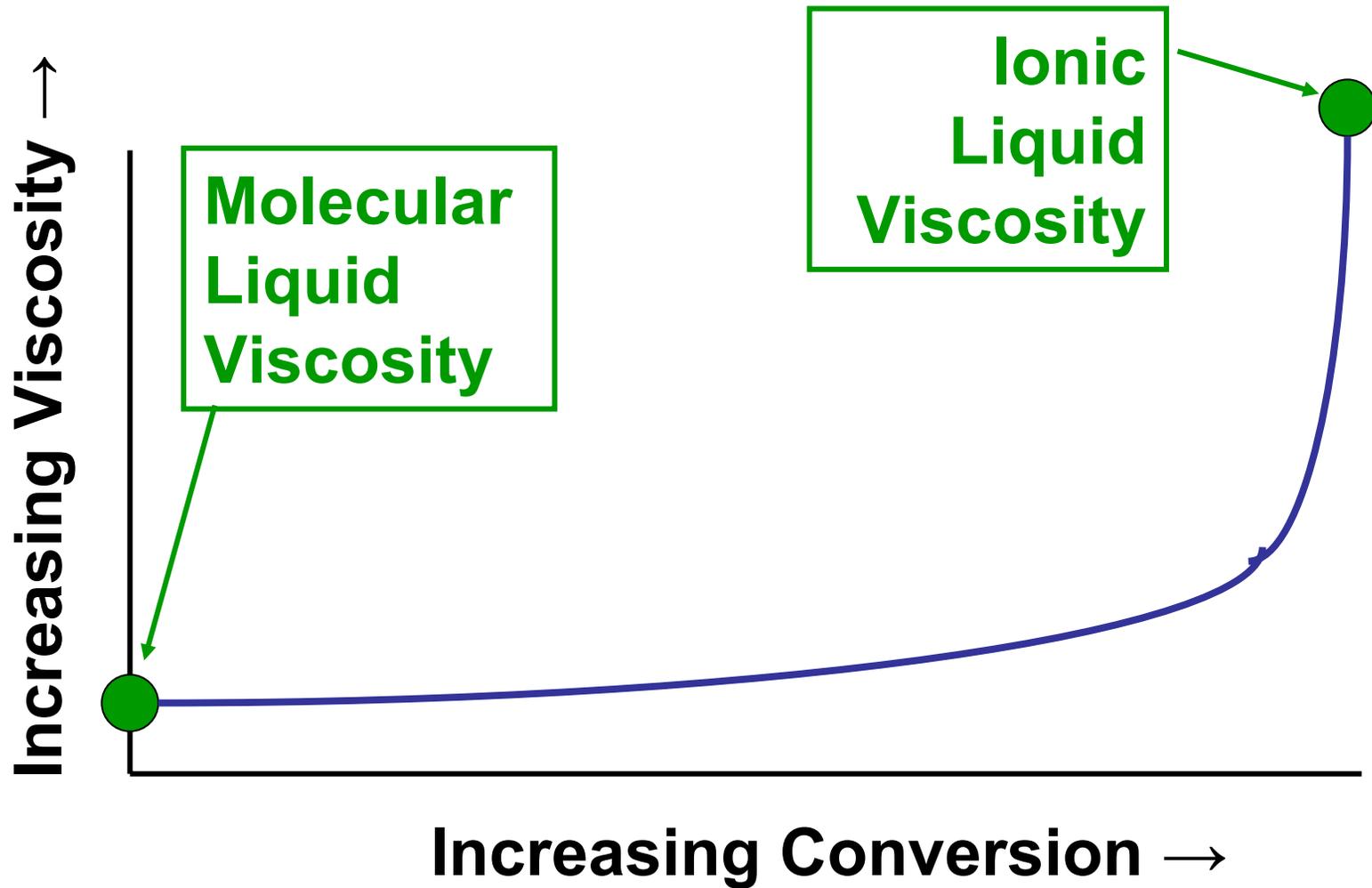
- Ease of Assembly, Operation
- Low Volume, High Surface RevIL
- Facile Flow of CO₂



But What About Viscosity?

- Viscosity of ILs Can be Quite High
- Rate of Transport of CO₂ Will Depend on Viscosity
- But, Viscosity Can Be Greatly Reduced

Viscosity Change for RevIL Formation is Highly Nonlinear



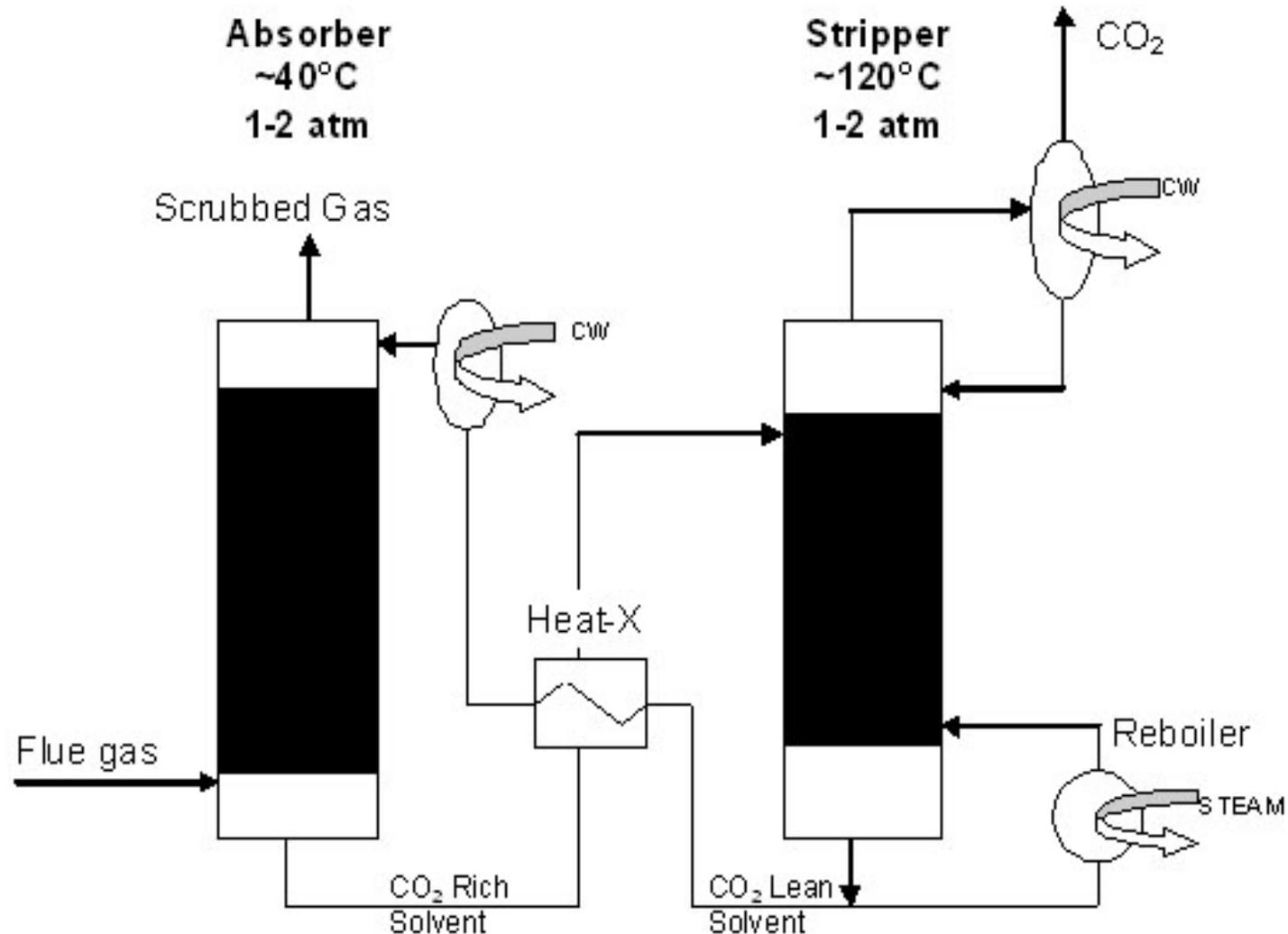
Dealing with Liquid Viscosity

- RevIL Viscosity Can Be Greatly Reduced
- Viscosity Change vs. Conversion is Nonlinear
 - ✓ Viscosity High Only for >95% Conversion
- Impurities Cut Viscosity Drastically
 - ✓ Water, Dissolved Gases
- Silylation Reduces Viscosity
- Goal: Viscosity not a Barrier to Transport

Path Forward: Economics and Design

- Existing MEA Design As Initial Template
- Optimal Solvent Candidate
- Measured Thermodynamics and Rate Data
- Optimize Processing Conditions
- Determine Economic Viability Of Process

Process Flow Diagram for Typical Solvent CO₂ Scrubbing System

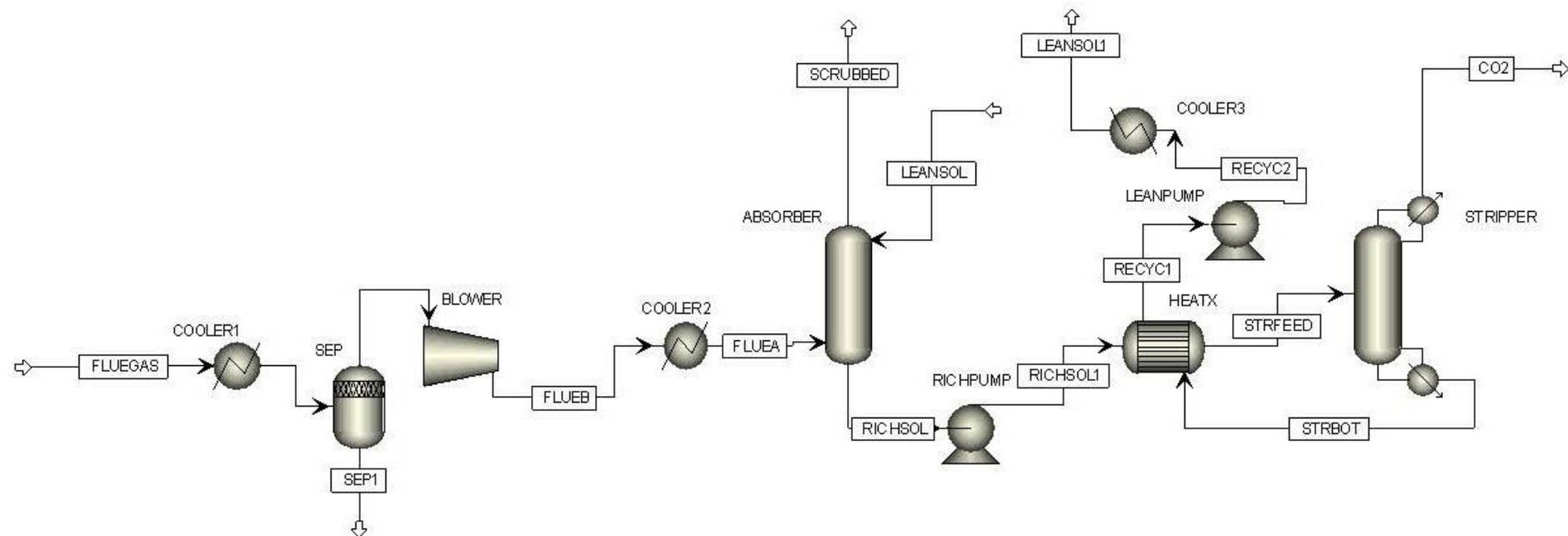


Energy Requirements

- Energy Removed
 - ✓ Heat of Adsorption of CO₂
 - ✓ Cooling of Exit Stream
- Energy Added
 - ✓ Heat of Desorption of CO₂
 - ✓ Makeup for Losses in Heat Transfer

ASPEN Flow Sheet for Process

- Industry Standard Design Software
- Permits Process Alternatives, Optimization
- Calculates Flows, Rates, Energy, Economics



Structure/Property Relationships

- Empirical Examples: Hammett Equation, Kamlet-Taft
- Goal: Effect of Structure on Properties
- Change Structure
 - ✓ Substituent Groups
 - ✓ Chain Length
- Assay Effect on Properties
 - ✓ Equilibrium Constants
 - ✓ Heat of Reaction
 - ✓ Transport – i.e. Viscosity

Final Process Optimization

- Solvent with Optimum Balance of Properties
 - ✓ Synthesize and Characterize
 - ✓ Use in Process Design
 - ✓ Determine Best by Energy, Economics
- Optimum Solvent
 - ✓ Demonstrate on Lab Scale
 - ✓ Design Pilot Scale Process
 - ✓ Develop Scalable Process for Synthesis
- Bottom Line: Superior Process for CO₂ Capture from Coal-Fired Power Plants

Additional Benefits of Project

- Education
 - ✓ Postdoctoral Students, PhDs, BS Students
 - ✓ Chemical Engineering and Chemistry
 - ✓ Technical Skills Related to Energy Issues
 - ✓ Critical Thinking About Energy Issues
- Other Potential Applications
 - ✓ CO₂ Capture from Combustion
 - Other Fossil Fuels
 - Biofuels
 - ✓ CO₂ Capture from Fermentation